THE TESTING OF CATALYSTS FOR ALKANE ACTIVATION*

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Introduction

Low oil prices have caused a decrease in the exploration for and development of new oil reserves in the United States. This, combined with an increase in U.S. oil consumption, has resulted in an increased dependence on foreign oil. In June 1986, 40% of the oil used in the U.S. was supplied by foreign sources as compared to 32% in 1983 (1); it is likely that this dependence on foreign oil will continue to increase. This leaves the U.S. vulnerable to sudden, drastic fluctuations in our liquid fuel supply. To minimize this dependence on foreign oil, it is necessary to find new sources for liquid fuels. One potential new source is methane, which makes up about 90% of natural gas. Methane can be partially oxidized to alcohol that could be used directly as liquid fuel or converted to gasoline by Mobil's methanol to gasoline process (2). Economic analyses (3) of potential processes for the conversion of methane to liquid fuel have shown that the use of partial oxidation to form methanol, in contrast to existing conventional methods of forming methanol from syngas, could make a methane to gasoline process economically feasible. Research is needed, however, to find catalysts that are capable of oxidizing methane to methanol with high conversions and high selectivities.

Most work performed on methane partial oxidation has used metal oxide catalysts at high temperatures and pressures (4-6). These studies have shown that catalytic oxidation of methane to methanol is possible, but conversion and selectivity are low. Liu, et. al. (7) have shown that Mo supported on silica is an effective catalyst for the partial oxidation of methane to methanol and formaldehyde when nitrous oxide is present as the oxidant. At a conversion level of 3%, the combined selectivity to CH_3OH and HCHO was 78%, with CO being the principal other product. Using ^{3}Li-doped MgO at a temperature of approximately 500^{o}C, Driscoll, et. al. (8) were able to show that methyl radicals were formed when methane was passed over the surface of this catalyst. The surface methoxide ions were converted to methanol by reacting with water in the system. The mechanism was similar to the one proposed for the partial oxidation of CH_4 over a Mo/SiO_2 catalyst (7).

Watson and Parshall (9-11) have reported that organolanthanide complexes can react with the C-H bond as shown by isotope exchange reactions using labeled methane. In this case, the catalyst was a dicyclopentadienyl methyllutetium compound. It was proposed that an electrophilic reaction took place between methane and the electron-deficient lanthanide complex.

Janowicz, et. al. (12) have shown that an iridium complex can convert alkanes into hydridoalkylmetal complexes, and that the insertion reaction proceeds through a three-center transition state.

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The hydrido products can then be converted to functionalized alkyl halides by treatment with mercuric chloride followed by halogens. Analogous rhodium complexes were shown to undergo similar C-H insertions, but the products were less stable than with the iridium complexes (12). Jones and Feher (13,14) have also shown that alkane C-H bonds can be activated by homogeneous Rh(I) compounds.

Methane can be selectively converted to methanol biochemically via a monooxygenase enzyme (15). Organisms capable of utilizing methane as their sole carbon and energy source are called methanotrophs. In the organism Methylococcus capsulatus, the monooxygenase enzyme has been shown to be capable of utilizing a variety of alkanes, alkenes, ethers, alicyclic compounds, etc. (15). The soluble methane monooxygenase from M. capsulatus was resolved into three fractions by ion exchange chromatography, but the molecular structures are unknown.

Several other naturally occurring enzymes, such as cytochrome P450 (16), can also catalyze the conversion of alkanes to alcohols at low temperatures and pressures. In an attempt to mimic the activity of these enzymes, we have initiated a program to tailor-make catalysts for the direct conversion of methane to methanol. Our work focuses on the use of metalloporphyrins, and relies on computer-aided design to guide the synthesis of novel catalytic materials. The molecular design techniques are being combined with structural studies (17) of biological catalysts to identify the important characteristics of the active site, the development of activity and selectivity tests to determine structure-activity relationships, and the synthesis of designed catalysts.

Porphyrins are being used because they are present in enzymes that perform C_1 chemistry (methyl reductase, methyl transferase), have versatile structures that can be controlled, and can be synthesized with many different metals. Porphyrins have also shown significant activity for oxidation of long chain alkanes (C5+) (18,19).

The objective of this paper is to describe the catalyst activity and selectivity tests we are developing and to report on the results of testing several commercially available porphyrins. To get structure-activity relationships, it is necessary to develop several different activity tests using alkanes with varying chain lengths. We started with a cyclohexane test using previously reported conditions (20) so that our results could be compared to literature results. Additional tests we have developed to date use hexane and butane as reactants. In the future, tests will be developed using ethane and methane as reactants.

Experimental Procedures

Materials

The catalysts used in this work included iron tetraphenyl porphyrin (FeTPPCl), manganese tetraphenyl porphyrin (MnTPPCl) and iron pentafluorophenyl porphyrin ($FeTF_5PPCl$). The first two catalysts were obtained from Porphyrin Products and the third from Aldrich. Methylene chloride (99+%) was used as the solvent in all tests. The oxidant was iodosylbenzene (C_6H_5IO) prepared from the reaction of iodosobenzene diacetate with NaOH (21). The alkanes used for the various tests were cyclohexane (99+%), hexane (99%), and butane (99.5%).

Reaction Conditions

Reactions with cyclohexane and hexane were performed in the liquid phase in an argon atmosphere glove-box. Each run had 1.4 cm^3 solvent and 0.6 cm^3 cyclohexane (or 0.7 cm^3 hexane). The ratio of reactant:oxidant:catalyst was 1100:20:1 (20) on a mole basis. These reactions were carried out at atmospheric pressure and ambient temperature (about 30°C in the glove-box) for 2 hours. Reactants were stirred at 1000 rpm.

The oxidation of butane was carried out under 5 psig pressure by bubbling butane at a flow rate of about 12 cm^3/min through a solution containing 2 cm^3 methylene chloride, 0.005 mmol catalyst, and 0.1 mmol oxidant. A condenser was attached to the reactor to minimize the loss of methylene chloride. The condenser temperature was set at 7°C so that butane condensation did not occur. At this temperature, small quantities of methylene choride vaporized so that additional solvent was added during the run to maintain constant volume. The reaction temperature was 19°C. After 6 hours, the flow of butane was stopped, the pressure gradually released, and the excess butane was allowed to outgas from the methylene chloride prior to analysis of the products.

Product Analyses

Oxidation products were identified using GC/MS techniques and quantified using capillary column gas chromatographic techniques with commercially available compounds as standards. Product yields are reported on the basis of the amount of oxidant added to the reactor.

Catalyst Characterization

The porphyrins were analyzed using UV-vis spectroscopy. Spectra were taken of both as received and used porphyrins to determine if any degradation of the porphyrin occurred during reaction.

Results and Discussion

Cyclohexane tests were run first in order to compare our results with published values (20). Initial runs used FeTPPCl. Tests with iodosylbenzene, prepared using previously reported procedures (21), resulted in low cyclohexanol yields, which were thought to be due to a high concentration of contaminants in the oxidant. Infrared (IR) spectra of the oxidant showed the presence of iodobenzene (C_6H_5I). Other phases could not be identified. Extensive cleaning using water and chloroform was carried out; the IR pattern of the product showed a significant decrease in the amount of iodobenzene present. The results we obtained for FeTPPCl and $FeTF_5PPCl$ with this purified batch of oxidant are shown in Table 1. The reported cyclohexanol yields (20) were 10.1% for FeTPPCl and 66.6% for $FeTF_5PPCl$. Our yields for both porphyrins are significantly higher than the literature values suggesting that we may have prepared a purer oxidant.

An additional test performed with MnTPPCl showed a much greater cyclohexanol yield than obtained with FeTPPCl. UV-vis analyses of the three catalysts before and after reaction showed that the FeTPPCl degraded during reaction, whereas the $FeTF_5PPCl$ and MnTPPCl showed no significant degradation. The extent of FeTPPCl degradation and the cyclohexanol yield from the run with FeTPPCl as a function of time are shown in Figures 1 and 2. A comparison of the results in these two figures indicates that some reaction still occurred even after the porphyrin was completely degraded. A test carried out with

reactant, oxidant and solvent, but no porphyrin, did not yield any cyclohexanol. This indicates that the iron species resulting from the degradation had some activity. The cause of the higher activity of MnTPPCl as compared to FeTPPCl is not definitively known. It could be entirely due to the degradation of the FeTPPCl or could be partially due to FeTPPCl degradation and partially due to differences in the activities of the two metals. This cannot be proven from these runs. Additional studies are being performed to determine the effects of different metals on catalyst activity.

The main structural difference between FeTPPCl and $FeTF_5PPCl$ is the replacement of hydrogens with fluorines on the phenyl rings. Steric and electronic effects of the fluorines prevent catalyst degradation to produce a more stable catalyst. The fluorines may also cause the catalyst to be more active (20). Runs with MnTPPCl and $FeTF_5PPCl$ that were carried out for about 16 hrs did not show any increase in yield beyond the first two hours, suggesting that the reactions might be limited by the amount of oxidant remaining. It has been suggested (20) that the oxidant can be further oxidized by an Fe-oxygen intermediate species of the porphyrin to give iodoxybenzene ($C_6H_5IO_2$) during these reactions. The iodoxybenzene is not an oxidant. We are currently performing studies to determine the fate of the iodosylbenzene in these reactions.

Activity testing with hexane was performed under the same conditions as with cyclohexane so that yields could be compared. Results for this test are shown in Table 1. The total hexanol yield is lower than the total cyclohexanol yield under the same conditions. The hexanol from the run with $FeTF_5PPCl$ consists of 1% 1-hexanol, 28% 2-hexanol and 27% 3-hexanol. These results show that selectivity to the 1-hexanol is very low and the total yield has decreased in going from the cyclic compound to the straight chain. The decrease in the yield of the 2- plus 3- alcohols in the hexane run, as compared to the cyclohexanol yield with the same catalyst, is proportional to the number of methylene groups. Hexane has 4 secondary carbons whereas cyclohexane has 6, and the yield of 2- plus 3- hexanols is 2/3 of the yield of cyclohexanol.

The run with butane yielded 35% butanol consisting of 34% 2-butanol and 1% 1-butanol. The concentration of butane in the methylene chloride under the test conditions was measured using Raman spectroscopy. The results showed that there was about 8% butane (on a mole basis). This is significantly lower than the 20% hydrocarbon present in the reactions with cyclohexane or hexane. The results of the tests with cyclohexane and hexane cannot be directly compared to the results of the butane tests because of the lower reactant concentration and the differences in reaction times and temperatures. Therefore, additional testing is being carried out to enable this comparison.

Conclusions

The results of the cyclohexane tests carried out for longer times indicate that it is necessary to determine what happens to the oxidant during the reaction, since the results suggest that oxidant is depleted even at low alcohol yields. If a more effective oxidant is found, yields should be significantly higher. The results with butane suggest that we may have a good test procedure for use with shorter chain alkanes. To be able to compare results from tests using cyclohexane and hexane to butane (and to future tests with ethane and methane), it will be necessary to determine the effects of different

reactant concentrations and different reaction times and temperatures.

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Table 1. Yields of alcohols reported as a percent of the initial oxidant input to the reactor.

REACTANT	CATALYST	TOTAL YIELD	1-ALC* YIELD	2-ALC YIELD	3-ALC YIELD
Cyclohexane	FeTPPCl	14			
	MnTPPCl	42			
	$FeTF_5PPCl$	84			
Hexane	$FeTF_5PPCl$	56	1	28	27
Butane	$FeTF_5PPCl$	35	1	34	

* ALC = alcohol.

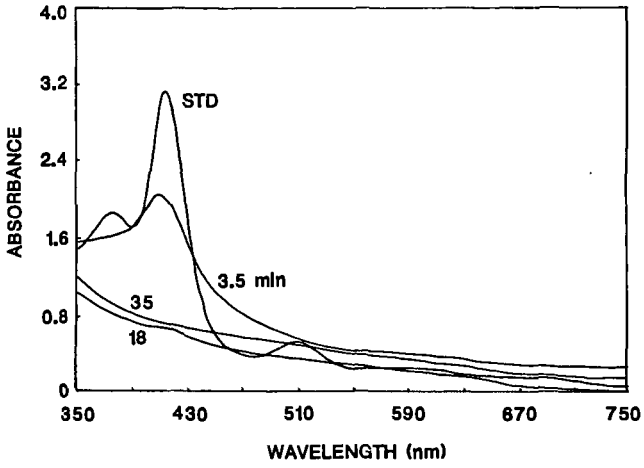

Figure 1. Comparison of UV-vis spectra of FeTPPCl (STD) with catalyst removed (at 3 times) from a reaction with cyclohexane.

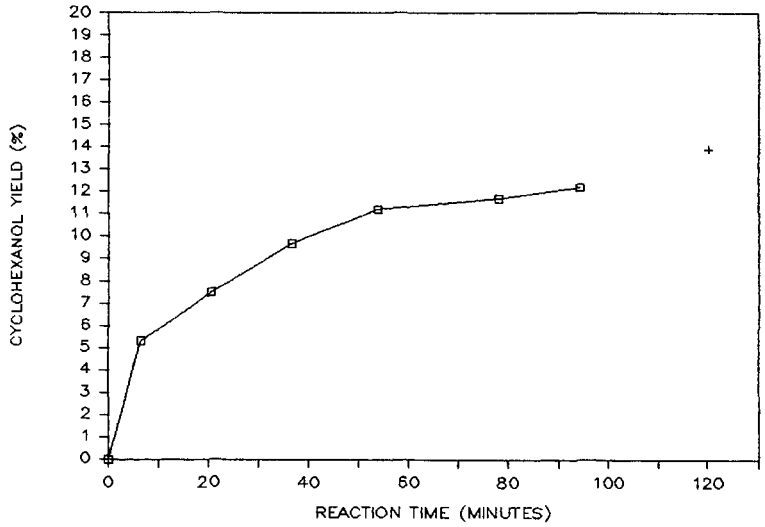

Figure 2. Cyclohexanol yield vs. run time. Catalyst = FeTPPCl. □ = samples pulled from reaction using a syringe (manual injection into GC). + = sample removed from reactor after end of run (automatic injection into GC).